

Figure 14A-2. Conceptual end view of cassette placement in a potroom roof.

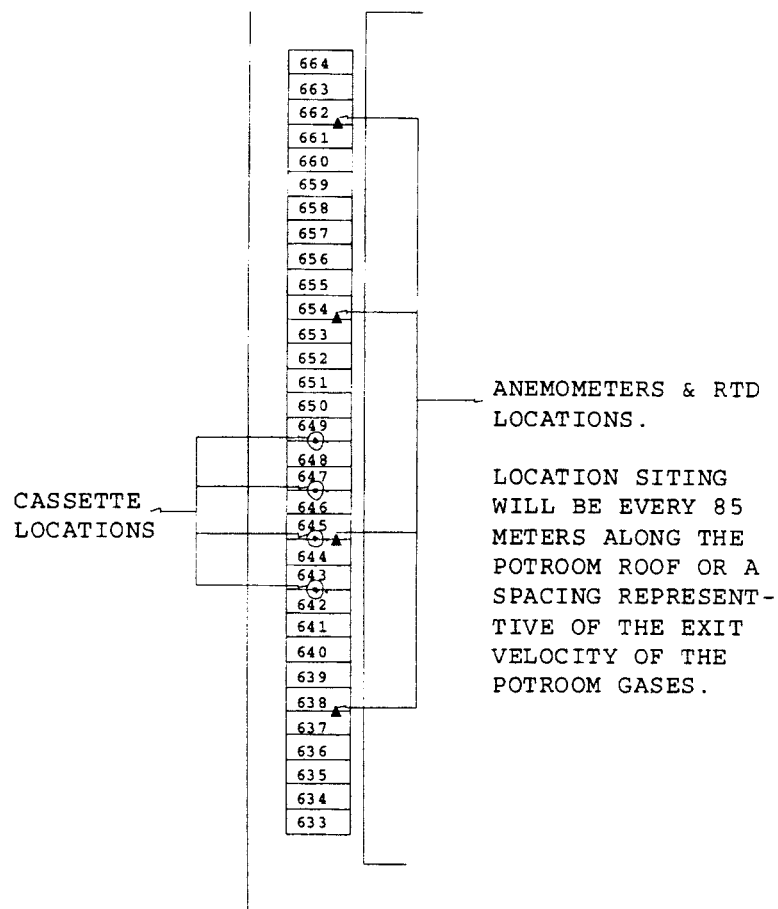


Figure 14A-3. Conceptual side view of positions of cassettes, anemometers, and RTDs in a typical half of a potroom.

Note: This drawing does not reflect other potentially acceptable arrangements.

**METHOD 15—DETERMINATION OF HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE EMISSIONS FROM STATIONARY SOURCES**

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance.

Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of gas chromatography techniques.

**1.0 Scope and Application**

**1.1 Analytes.**

Analyte	CAS No.	Sensitivity (See Sec 13.2)
Carbon disulfide [CS <sub>2</sub> ] .....	75–15–0	0.5 ppmv
Carbonyl sulfide [COS] .....	463–58–1	0.5 ppmv
Hydrogen sulfide [H <sub>2</sub> S] .....	7783–06–4	0.5 ppmv

**1.2 Applicability.**

1.2.1 This method applies to the determination of emissions of reduced sulfur compounds from tail gas control units of sulfur recovery plants, H<sub>2</sub>S in fuel gas for fuel gas combustion devices, and where specified in other applicable subparts of the regulations.

1.2.2 The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods for determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample-line loss criteria are met.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

2.1 A gas sample is extracted from the emission source and diluted with clean dry air (if necessary). An aliquot of the diluted sample is then analyzed for CS<sub>2</sub>, COS, and H<sub>2</sub>S by GC/FPD.

**3.0 Definitions. [Reserved]**

**4.0 Interferences**

4.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the probe, filter box, and connections, and by maintaining the SO<sub>2</sub> scrubber in an ice water bath. Moisture is removed in the SO<sub>2</sub> scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below

the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO<sub>2</sub>). CO and CO<sub>2</sub> have substantial desensitizing effects on the FPD even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting CO and CO<sub>2</sub> before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO<sub>2</sub> in the diluent gas. The CO<sub>2</sub> level should be approximately 10 percent for the case with CO<sub>2</sub> present. The two chromatograms should show agreement within the precision limits of Section 13.3.

4.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling system can lead to blockage of the particulate filter. This problem can be minimized by observing the filter for buildup and changing as needed.

4.4 Sulfur Dioxide (SO<sub>2</sub>). SO<sub>2</sub> is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO<sub>2</sub> scrubber described in Section 6.1.3 will effectively remove SO<sub>2</sub> from the sample.

4.5 Alkali Mist. Alkali mist in the emissions of some control devices may cause a rapid increase in the SO<sub>2</sub> scrubber pH, resulting in low sample recoveries. Replacing the SO<sub>2</sub> scrubber contents after each run will minimize the chances of interference in these cases.

**5.0 Safety**

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test to establish appropriate safety and health practices and determine the applicability of regulatory limitations to performing this test.

### 6.0 Equipment and Supplies

6.1 Sample Collection. See Figure 15-1. The sampling train component parts are discussed in the following sections:

6.1.1 Probe. The probe shall be made of Teflon or Teflon-lined stainless steel and heated to prevent moisture condensation. It shall be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. The probe described in Section 6.1.1 of Method 16A having a nozzle directed away from the gas stream is recommended for sources having particulate or mist emissions. Where very high stack temperatures prohibit the use of Teflon probe components, glass or quartz-lined probes may serve as substitutes.

6.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO<sub>2</sub> Scrubber. Three 300-ml Teflon segment impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3-mm (1/8-in.) ID and should be immersed to a depth of at least 50 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C. The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO<sub>2</sub> scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO<sub>2</sub> scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 13-mm (1/2-in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line-loss test is acceptable.

6.1.5 Sample Pump. The sample pump shall be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel. It must be capable of approximately a 9:1 dilution of the sample.

6.2.2 Gas Chromatograph (see Figure 15-2). The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature  $\pm 1$  °C.

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature  $\pm 1$  °C.

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of  $10^{-9}$  to  $10^{-4}$  amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.5 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.6 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas. The GC shall be calibrated with the sample loop used for sample analysis.

6.2.2.7 GC Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H<sub>2</sub>S, COS, and CS<sub>2</sub>. To demonstrate that adequate resolution has been achieved, a chromatogram of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard must be submitted. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero ( $\pm 5$  percent) in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration System (See Figure 15-3). The calibration system must contain the following components:

6.3.1 Flow System. To measure air flow over permeation tubes within 2 percent. Each flowmeter shall be calibrated after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by more than 5 percent, the completed test shall be discarded. Alternatively, use the flow data that will yield the lowest flow measurement. Calibration with a wet-test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.2 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C.